

International Society for the Advancement of Supercritical Fluids
(I.S.A.S.F.)

7758



PROCEEDINGS

The 4th International Symposium on Supercritical Fluids

Volume B

Phase Behavior ~ Thermodynamics
and Equilibria and Mass Transfer
(PEQ) (TMT)

Sendai, Japan

11 - 14 May, 1997

Supplied by U.S. Dept. of Agric.,
National Center for Agricultural
Utilization Research, Peoria, IL

Packed Column Fractionation of Glycerides using Supercritical Carbon Dioxide

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A mixture of monoacylglycerides (MAGs), diacylglycerides (DAGs) and triacylglycerides (TAGs) were fractionated using supercritical CO₂ in a packed column that was kept under thermal gradient conditions and operated semi-continuously. The feed material used, approximated a feed stream used in the industrial enrichment of MAGs, was composed of 48.7 wt% MAG, 46.3 wt% DAG, and 5 wt% TAG, having main acyl chain compositions of 6 wt% C16:0, 23 wt% C18:0 and 59 wt% C18:1. Fractionation of these glycerides was affected by both their interaction with CO₂ and respective vapor pressures. The resultant top product from the fractionation column had a MAG concentration higher than 90 wt% and no TAG, which is comparable to that produced by molecular distillation.

The effects of pressure and temperature gradient, on the separation efficiency and yields were investigated. Increasing column pressure from 17.2 MPa to 34.4 MPa increased yields of the top product, but decreased MAG concentration from 94 wt% to 56 wt%. At 20.7 MPa, a linear temperature gradient from the bottom to top of the column from 65 °C to 95 °C gave the best selectivity than the other temperature gradient schemes tested. Products having high concentrations of MAGs, DAGs and TAGs were obtained, sequentially, using a semi-batch operation mode.

Introduction

Surface active lipids having a wide range of applications in the food industry, where they are used for emulsification, starch complexing, aeration, as defoaming agents and as oil stabilizers. Monoacylglycerols (MAGs) of saturated and unsaturated fatty acids are the most commonly used emulsifiers in breads and other baked goods, reduced fat margarines and spreads, and instantized powders.

Monoglycerides are partial esters of glycerol containing higher molecular weight fatty acids. They are commonly produced by esterifying glycerol with fatty acids, by transesterification of triacylglycerols (TAGs) with glycerols or by enzymatic cleavage of TAGs. These reactions often produce a mixture of monoacylglycerols (MAGs), diacylglycerols (DAGs) and triacylglycerols (TAGs). Molecular distillation has commonly been used to manufacture high monoacylglycerol-containing emulsifiers from the reaction mixture. However, the use of a high vacuum and temperatures (usually more than 200°C) associated with molecular distillation, are problematic, leading to the possibility of alteration of some of the components and formation of undesired products [1,2].

Pure or modified SC-CO₂ may be used to separate nonpolar lipid components from polar moieties, or for the fractionation of lipid material having significant differences in molecular weight or vapor pressure. One advantage with SCF processes is that the fractionation of lipid mixtures may be accomplished if there are marked differences in either, mass, vapor pressure or polarity of the molecular constituents. A packed fractionation column amplifies these molecular differences by varying the solvent strength of the fluid through sequential pressure changes or via a longitudinal temperature gradient.

Studies have shown that the fractionation of polymers with respect to molecular weight, chemical composition, and back bone structure, as well as the purification of speciality monomers can be achieved using SF fraction [3,4,5,6]. There has been some research on fractionation of the lipid constituents of natural oils, and studies have demonstrated the potential of thermal gradient [7,8,9] or pressure gradient methods [10], and along with packed column fractionation methods toward this end [12].

When a mixture of glycerides is allowed to equilibrate with SC-CO₂, some of the glycerides dissolve in the CO phase, while some CO₂ dissolves in the glyceride phase. Such a system, consisting of a glyceride-rich phase and a CO₂-rich phase, may be considered as a pseudo-binary system. The distribution of glyceride species between the two phases is the basis of separation and fractionation. This distribution depends on the glycerides vapor pressure and the CO₂-glyceride and glyceride-glyceride interactions. These interactions are influenced by differences in molecular weight, polarity and chemical structure of glyceride species. Distribution of the glyceride species between the two phases can be approximated by determining their interphase distribution coefficient. For a given mixture, the distribution coefficient is a function of solvent strength (i.e., density of CO₂) and temperature. A theoretical treatment of the equilibrium relationships of a multi component two-phase system is complicated. The principles involved are essentially the same as a binary system, except that one must account for solute-solute interactions.

In this paper, we describe the fractionation of glycerides with respect to their vapor pressure and molecular weight. Glyceride mixtures of mono, di- and triglyceride were selected for this study since they are readily available and can be used to study the influence of molecular weight,

polarity and fatty acid composition on the fractionation of glycerides. This study identifies the important process variables and optimizes conditions that allow the attainment of high separation efficiency.

Materials and Methods

The feed material used for this study was a mixture of mono-, di-, and triglycerides called Myvatex Mighty Soft™ Softener, obtained from Eastman Chemical Company (Kingsport, Tennessee). The feed material used, approximated a feed stream used in the industrial enrichment of MAGs, composed of 47.5wt% MAG, 45.5 wt% DAG, and 5.7 wt% TAG, having main acyl chain compositions of 9.8 wt% C16:0, 41.1 wt% C18:0 and 41.9 wt% C18:1 and 9.6 wt% C18:2. Welding-grade carbon dioxide used in the experiments was obtained from National Welding Supply (Bloomington, IL) in 25 kg gas cylinders.

The supercritical fluid fractionation was performed in a column containing a distillation packing, along which temperature (density) gradient was maintained. The pilot-scale column included a preheater and four separately heated zones, each having an internal diameter of 1.43cm, and a height of 41.5 cm. A schematic diagram of the packed column supercritical fluid fractionation system is shown in Figure 1. The column has a total height of 164 cm and a volume of 260 cm³ and is packed with stainless steel packing, Pro-Pak (Scientific Development Company, State College, PA). Each zone was heated to the desired temperature using Glas Col heating mantles (Glas Col, Inc., Terre Haute, IN) and the temperature was recorded by Type J thermocouples attached to the column wall. Wall temperature for each zone was maintained to $\pm 1^\circ\text{C}$ and independently controlled by a Model CN4600 controller (Omega Engineering, Inc., Stamford, CT).

The column was allowed to thermally equilibrate for about one a half hour before the feed was introduced. The feed mixture was melted and a liquid metering pump (Haskel MS-188) was used to feed the mixture into the column. For each run, 70 ml of feed was pumped in; an amount equal to the void space in Zone 1. Carbon dioxide was introduced from a commercial cylinder, through a filter, at about 60 bars to a Haskel gas booster pump (Model ACT 62/152, Haskel Inc., Burbank, CA, having a capacity of 690 bars and an output 240 cm³/min). The pressurized column was then equilibrated for more than one hour before the outlet valve was opened.

As shown in Fig. 1, carbon dioxide enters the preheater and then passes through the column upward along the temperature gradient. The solute-loaded SC-CO₂ flows up the column through the zones of increasing temperature. The fluid leaving the column was expanded across a micrometering valve (Autoclave Engineers, Inc. Eric, PA, Model 30VRMM4812) permitting fractionated products to be collected in the separator flasks. Finally the gas stream passed through a dry test meter (Singer, Model DTM-115, American Metering Division, Philadelphia, PA) used to measure the total gas volume and was vented to the atmosphere.

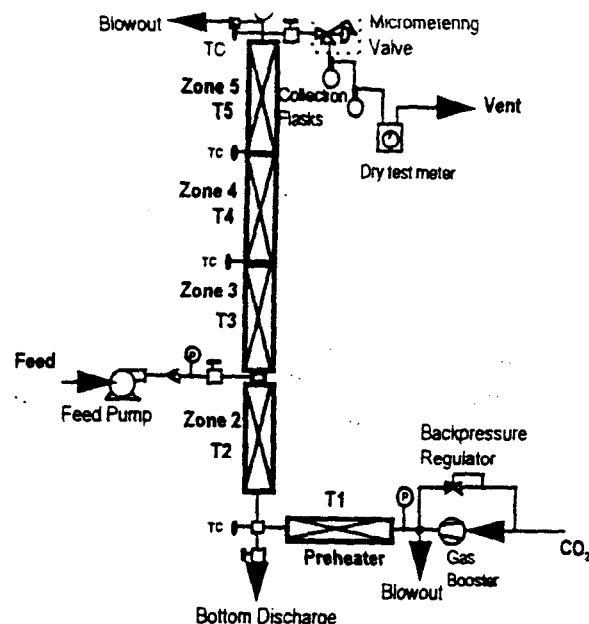


Figure 1. Schematic diagram of the packed column fractionation system.

Experiments were designed to study the effect of process parameters on the separation efficiency and yield of the fractionated product. Process parameters including the effect of temperature gradient, pressure (density), solvent flow rates, and feed composition. Experiments were conducted at pressures from 17.2 to 34.5 MPa, which encompasses the density range from 400 to 750 kg/m³ at the average column temperature. Expanded CO₂ flow rate from 2 to 5 L/min allowed retention times for the SC-CO₂ in the column of 55 min to 18 min, respectively. The composition of the top and bottom products were analyzed using a Lee Scientific Series II, Model 600 supercritical fluid chromatograph that was equipped with a flame ionization detector (Dionex, Inc. Salt Lake City, UT).

Results and Discussions

The range of molecular weights of the MAGs, DAGs and TAGs were 274 to 354, 456 to 616, and 639 to 878 amu, respectively. The vapor pressures of MAGs are 3 to 5 orders of magnitude higher than that of DAGs and TAGs, and are affected by both the length and the saturation of the fatty acids [13].

Product Composition Profiles. For a semi-batch operation conducted at a 20.7MPa, the composition of the extract removed from the column during each time interval is shown as a function of the weight percent collected (Figure 2). The composition of the liquid phase in the column was calculated by subtracting the extracted amount from the initial feed. Initially the extract was richer in MAGs than the liquid composition remaining in the column.

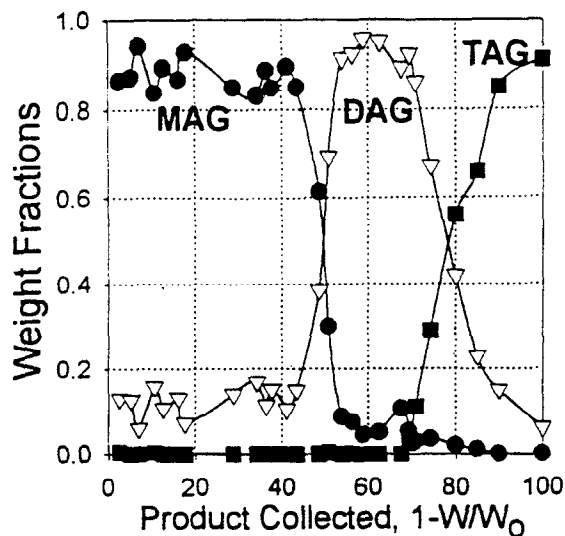


Figure 2. Transient composition profiles of product fractions.

Overtime, the liquid remaining in the column was stripped of MAGs and the extract composition changed gradually. The MAGs concentration in the extract remained high until 50% of the initial feed mass has been collected. The extract became sequentially richer in DAGs, and TAGs as the contents of the column was depleted

Influence of Pressure: The effects of pressure were examined by keeping the column temperature gradient for the four zones at 65, 75, 85 and 95°C, respectively, and CO₂ at a flow rate of 2 L/min (expanded fluid). Higher pressure results in an increase in solvent power, and increase in solubility of glycerides. As the pressure increases the MAG concentration in the top product dropped from 94% MAG at 18 MPa to 58% MAG at 34.5 MPa (Figure 3).

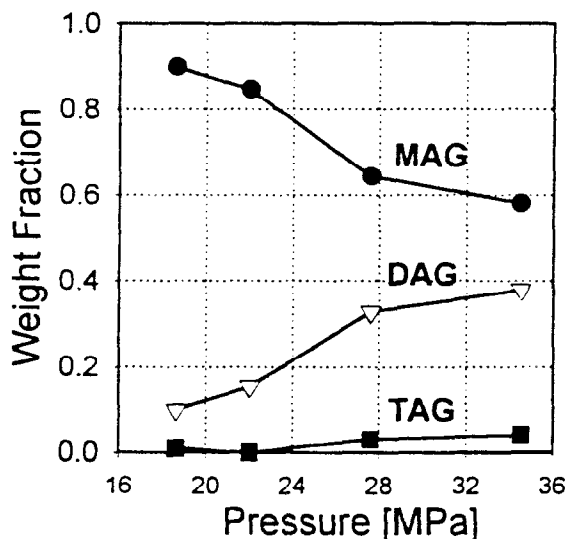


Figure 3. Effect of pressure on top product yield.

As the pressure increases at constant temperature, the solubility of components having lower volatilities (i.e., di- and triglycerides) increasingly solubilized in the SC-CO₂ [14]. Therefore, such an increase in solvent strength makes the process less selective.

The increase in pressure also resulted in higher top product yield. The top product yield decreased from 15 gm/kgCO₂ to 2 gm/kgCQ as the pressure decreased from 34.5 MPa to 17.2 MPa (Figure 4). Further decrease in pressure lowered the yield significantly to the extent that at pressures below 15.2 MPa there was no measurable yield collected.

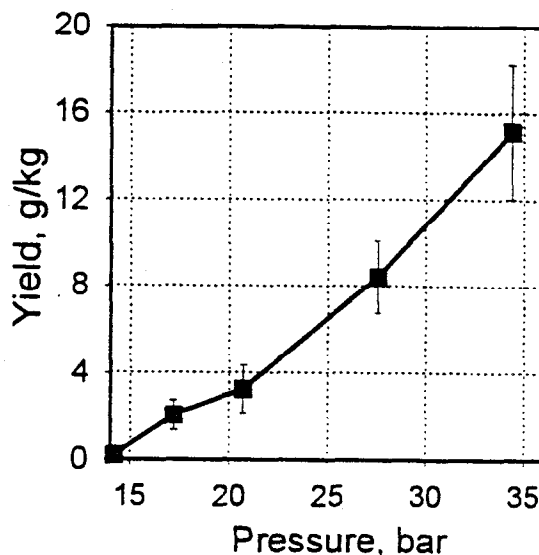


Figure 4 Influence of pressure on top product yield

Influence of the Temperature Gradient: Determining the most effective temperature gradient along the column was done at a pressure of 20.7 MPa and CO₂ flow rate of 2 L/min. A pressure of 20.7 MPa gave high selectivity and sufficient solute for analysis. The low flow rate allows retention times for the solvent of more than 5 minutes in each zone and ensures that thermal equilibration is maintained within the column. Two constant temperature profiles, one at 65°C the other at 90°C, and one linear temperature gradient profile using a temperature interval of 65 to 95°C were used.

The extraction curves of a glyceride mixture at 20.7 MPa and CO₂ flow rate of 4 L/min is shown in Fig. 5. The slope of the extraction curve for the uniform temperature gradient of 90°C was close to that of the one with the linear temperature gradient of 65 to 95°C. This indicates that the rate of product leaving the top of the column depends on the upper zone temperature. The slope of the extraction curve for a uniform column temperature of 65°C was much higher than the other two temperature profiles (Fig. 5). This rate corresponds to the rate of product leaving the zone 2 of the column to the upper stripping-section of the column. Therefore, the internal reflux ratio may be calculated from the ratio of the difference of the bottom and top extraction rates to that of the top extraction rate.

For the column used in this study the internal length ratio for a linear temperature profile was estimated to be 4.3. Temperature gradients other than linear were also tested and their influences on the performance of the column were studied [13].

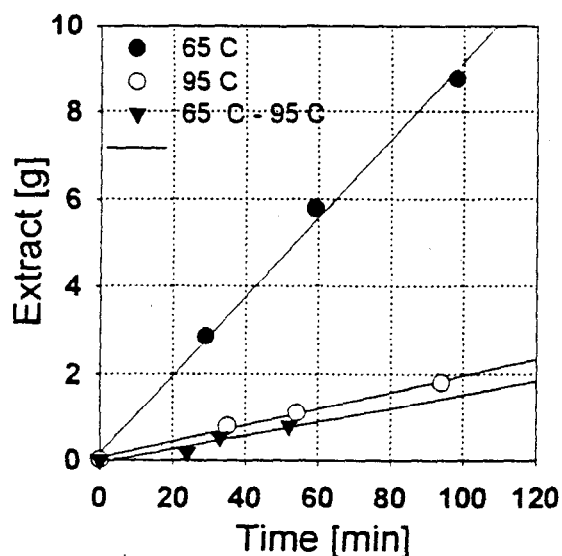


Figure 5. Extraction curves for glycerides at 20.7 Mpa.

Conclusion

Utilization of packed columns kept under a longitudinal thermal gradient employing supercritical carbon dioxide as a solvent have been shown to be effective for fractionating glyceride mixtures. Enrichment of MAG concentration as high as 90 wt.% can be obtained by optimizing the separation conditions. The best enrichment conditions were found to be a pressure of 20 MPa combined with a linear temperature gradient of 50 to 100°C on the column. Supercritical fluid fractionation of the described glyceride mixtures appears to be sensitive to pressure, but not to solvent flow rates.

Other process variables such as cosolvent addition to the CO₂ could enhance the supercritical fluid fractionation of glycerides[15]. This variable and the continuous, countercurrent operation of a thermal gradient fractionation tower under supercritical fluid conditions are currently being investigated in our laboratory for enrichment of glyceride mixtures derived from synthetic process conducted in supercritical media [16,17].

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